Variation of Some Properties of Tantalum Carbide with Carbon Content

Gilbert Santoro

Repr. from Trans. the AIME Met. Soc., v. 227, Dec. 1963 p 1361-1368 rep
pp. 1361-1368

In this study tantalum carbide filaments of various compositions in the fcc region were prepared by heating a tantalum wire in a measured amount of hydrocarbon vapor. Such properties as tensile strength, transverse-rupture strength, microhardness, lattice parameter, electrical resistivity, and magnetic susceptibility were measured as a function of carbon content. Some of these properties showed a maximum or a minimum between a carbon-to-tantalum molar ratio of 0.80 and 0.85, the composition range at which the color changes from metallic gray to gold.

THE recent literature has shown that in the large homogeneity range for the fcc phase of the Ta-C system there is a marked variation for such properties as microhardness,[1] electrical resistivity,[1,2] thermodynamic properties,[2,3] lattice parameter,[4-6] and superconductivity.[7] In addition to the technological interest of these variations within a single phase, important theoretical benefits may ensue from a continuous investigation of properties vs stoichiometry in tantalum carbide and other refractory defect compounds, for example the effect of the metal-metal distance and crystal structure upon bond formation and electronic structure.

Whether there is a similar variation of the tensile strength is of practical importance. Of theoretical interest would be the knowledge of how the magnetic susceptibility varies with carbon composition. Both of these properties, as well as the transverse-rupture strength, were determined for tantalum carbide filaments in the fcc phase region. The lattice parameter, the electrical resistivity, and the microhardness were also investigated and compared with values appearing in the literature.

EXPERIMENTAL PROCEDURE

Material Preparation. Tantalum carbide specimens of various carbon content were prepared by statically carburizing high-purity tantalum filaments in measured quantities of pure hydrocarbon gas. The filaments, which were 10 mil in diameter and 20 or 40 cm long, were heated by their own resistance at temperatures from 1800° to 2200°C using alternating current in some cases and direct current in others. Tantalum wire from two sources was used. One had a reported purity of 99.96 wt pct Ta. The ingot from which this wire was drawn had been electron beam-melted as the final step in its purification. The reported purity of the other wire, which was prepared by a powder metallurgical process, was 99.88 wt pct Ta. The impurities of both tantalum sources are listed in Table I. Spectrographic-grade toluene or research-grade propane was used as the source of carbon.

The apparatus for the carburization of the filaments is shown schematically in Fig. 1. The system was evacuated to 1×10^{-6} mm of Hg when using the electron beam-melted tantalum and to less than 1 μ when using the less-pure tantalum. Neither the difference in the base vacuum, nor in the hydrocarbon gas, nor in the tantalum filaments resulted in any detectable difference in the properties studied in this work. However, only the carbides prepared from the higher-purity tantalum were used in the magnetic-susceptibility determinations. Once the base vacuum had been reached, the system was flushed with the hydrocarbon and re-evacuated. For any desired composition of the carbide, hydrocarbon gas was allowed to leak into a constant-volume flask to a predetermined pressure. These pressures were measured by a Cartesian diver-type mercury gage with a range from 0 to 20 mm and with a scale expanded to nine times. The hydrocarbon gas was allowed into the reaction tube and the filament was quickly raised to the reaction temperature. The slack in the filament due to thermal expansion was taken up by drawing out the movable electrode with a screw mechanism. The filaments were kept at temperature from a few minutes to 200 hr. In the majority of cases the heating time was 6 hr. The reaction tube was cooled by cascading water on its outer surface. By means of an ammeter and a voltmeter the electrical resistance at the reaction

Table I. Analysis of the Tantalum Metals

Electron Beam-Melted Tantalum		Powder-Metallurgy Tantalum	
Element	Ppm	Element	Ppm
Nb	150	Nb	500
Al, Cu	<50	W	400
Fe	25	Fe	200
Mo	<25	C	100
C, Cr, Ni, Ti	<10		
H, N, O (total)	<17		

GILBERT SANTORO is Aerospace Technologist, National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio.

Manuscript submitted February 27, 1963. IMD

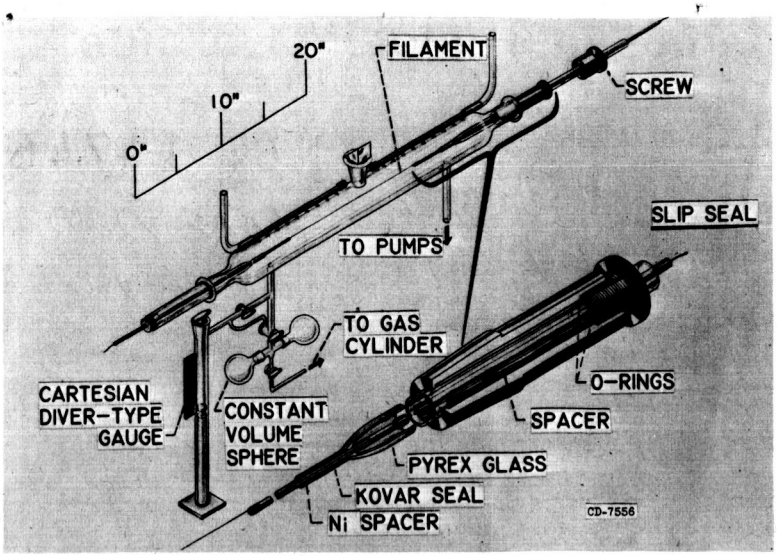

Fig. 1—Apparatus for preparing tantalum carbide of various carbon compositions.

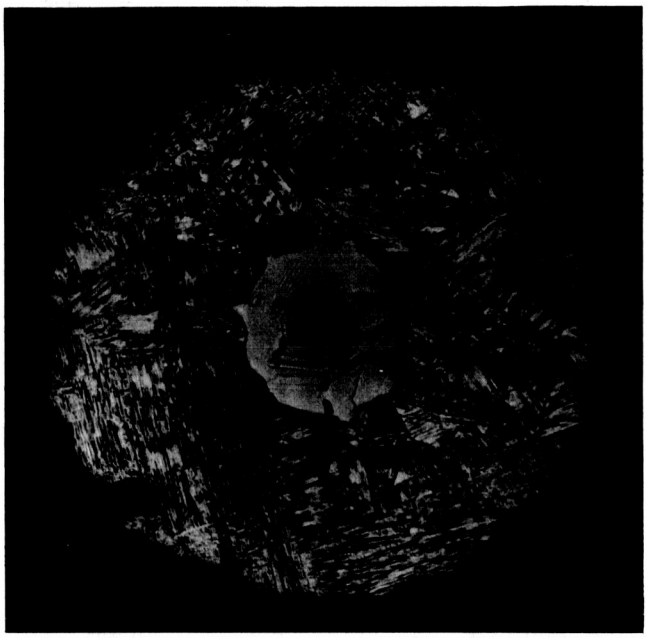

Fig. 2—Carburized tantalum filament X300. Reacted 6 hr at 2000°C. Molar ratio C/Ta = 0.68. Reduced approximately 9 pct for reproduction.

temperature was recorded as the carburization proceeded. The temperatures were determined by a calibrated optical pyrometer and the readings corrected for the absorption of the emitted light by the quartz port and the prism. An emissivity correction of 0.4 was used for all compositions.[9] When cooling, the filament was continuously adjusted so as to keep it taut. In this manner, over eighty carbide filaments of various carbon compositions were prepared. It was found from chemical analysis that the total carbon concentration was within $TaC_{x\pm0.03}$ of the precalculated value in the composition range $0.40 \leq x \leq 0.91$. A composition of only $TaC_{0.92}$ resulted when using the calculated amount of hydrocarbon for stoichiometry. The highest carbide that could be prepared by using an excess of hydrocarbon gas was $TaC_{0.98}$.

The uniformity of the carburization along the diameter of the wire was investigated by metallography, microhardness, and X-ray techniques. X-ray diffraction patterns of filament surfaces were compared with those after grinding the sample into a powder. Uniformity along the length was determined by X-ray diffraction and electrical-resistivity measurements made at various positions along the wire and by dividing the wire into two or three sections and analyzing each section for total carbon. For these sections the small quantity of material precluded duplicate analysis. In other specimens duplicate analyses were made for total carbon, but additional analysis for free carbon, nitrogen, oxygen, and hydrogen was not possible on the same filament. Other carbide filaments were analyzed for oxygen and hydrogen by hot extraction giving 34 and 3 ppm, respectively. No attempt was made to analyze for nitrogen although it should be of the same order of magnitude as the other gas impurities. All the carbon concentrations given in this report are for total carbon. The analysis was accomplished by combustion. The small quantity of sample precluded reliable free-carbon analysis.

From the highest carbide obtained down to $TaC_{0.70}$ the samples proved to be uniform radially and along the wire axis. Just below $TaC_{0.70}$ the cross section consisted of two concentric and distinct regions as in Fig. 2. At a concentration of about $TaC_{0.43}$ four different regions could be observed, as in Fig. 3. The carbon concentration in the multistructure samples was found by X-ray diffraction and microhardness to decrease toward the center of the cross section. Not every structure represented a pure phase. In some cases, it represented a primary phase and a small quantity of another phase, which appeared as very weak lines on the X-ray pattern. The carbon concentration along the entire length of the long wires varied less than $TaC_{x\pm0.01}$ down to an over-all composition of $TaC_{0.65}$. At an over-all carbon composition of $TaC_{0.45}$, the gradient was as high as $TaC_{x\pm0.05}$ over a 40-cm length. The

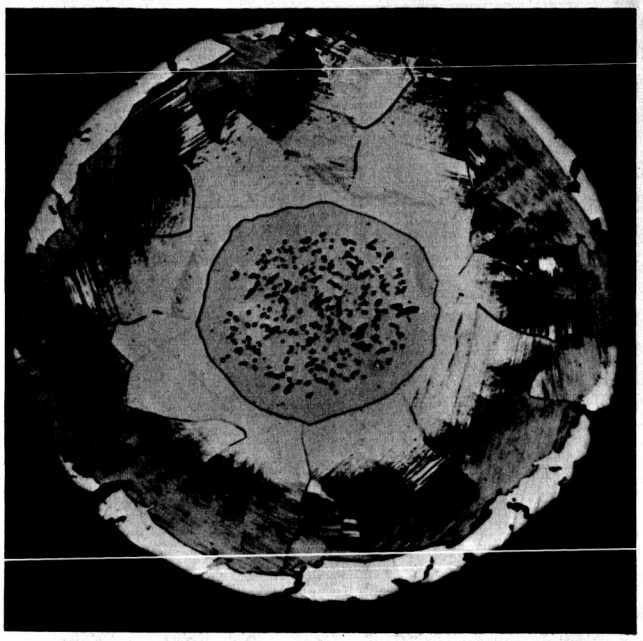

Fig. 3—Carburized tantalum filament X300. Reacted 6 hr at 2000°C. Molar ratio C/Ta = 0.43. Reduced approximately 3 pct for reproduction.

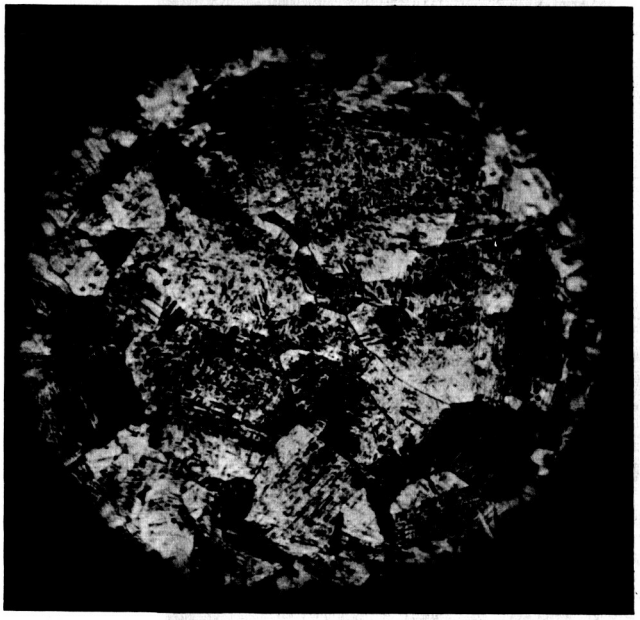

Fig. 4—Carburized tantalum filament X300. Reacted 17 hr at 2000°C. Molar ratio C/Ta = 0.73. Reduced approximately 3 pct for reproduction.

longitudinal concentration gradient was found not to be dependent on whether the current through the wire was alternating or direct. Table II gives the corresponding phases present for a number of compositions. Just below a composition of $TaC_{0.74}$ a uniform distribution of striations appears on the photomicrographs, see Fig. 4, and weak Ta_2C lines (hexagonal crystal structure) on the X-ray diffraction film. Above $TaC_{0.74}$ only TaC lines (NaCl-type crystal structure) occur and the photomicrographs are plain. Fig. 5 is a typical example. For this reason the investigation of the various properties

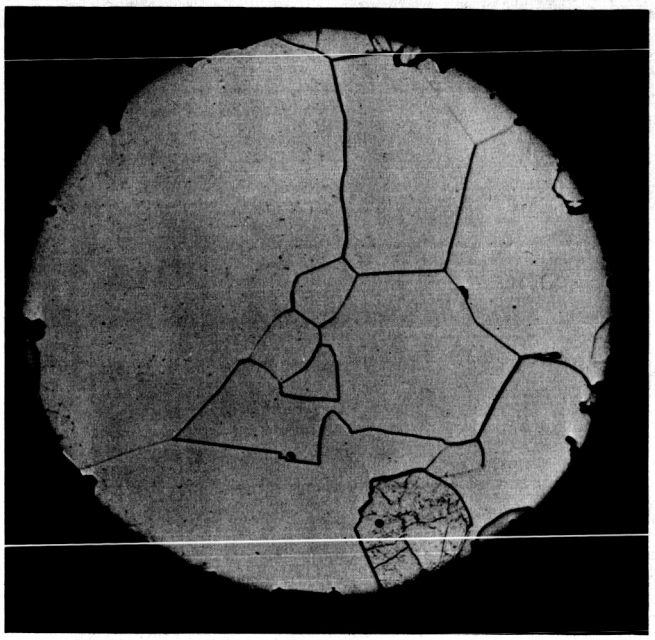

Fig. 5—Carburized tantalum filament X300. Reacted 6 hr at 2000°C. Molar ratio C/Ta = 0.91. Reduced approximately 10 pct for reproduction.

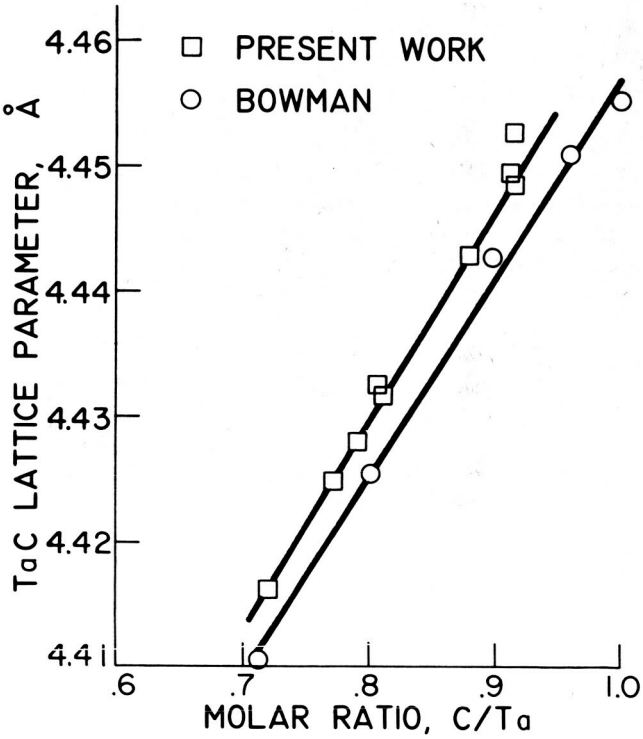

Fig. 6—Variation of TaC lattice parameter with composition.

studied here was not carried out much below $TaC_{0.74}$.

Fig. 6 shows the variation of the lattice parameter for TaC. The X-ray diffraction patterns were made with a 114.6-mm-diam Debye-Sherrer camera using Cu-K_α radiation. Probably the best values for the lattice parameter in the fcc phase were reported by Bowman,[4] Lesser and Brauer,[5] and Dolloff.[6] The purity together with the homogeneity of their samples exceed that of other workers and

Table II. Composition and Phases of Carbide Filaments Reacted at 2000°C

Composition, Molar Ratio C/Ta	Phases (by X-Ray Diffraction)	Description of the Structures
0.975 – 0.740	γ only	Appears as in Fig. 5
0.730 – 0.710	$(\beta) + \gamma$	Appears as in Fig. 4
0.680	$(\beta) + \gamma$	Fig. 2
0.675	$\beta + \gamma + (\zeta)$	—
0.520	$\beta + \gamma + (\zeta)$	—
0.430	$\alpha + \beta + (\gamma) + (\zeta)$	Fig. 3

γ – fcc (NaCl type), TaC.
β – hexagonal, Ta_2C.
α – bcc, Ta.
ζ – an unknown phase first reported by Lesser and Brauer.[5]
( ) – a few very weak lines on the X-ray film.

the data of these authors are in good agreement. Bowman's data also appears in Fig. 6. A comparison of the present work with that of Bowman's, in which free carbon was known to be absent, indicates that for the wire samples free carbon must either be nonexistent or very small. In addition, the examination of numerous photomicrographs of the filaments failed to reveal a structure which could be interpreted as occluded carbon flakes. The possibility of a radial carbon gradient as the cause for the difference in the two curves must be ruled out for two reasons. The X-ray diffraction patterns of the filament surface were identical with those after grinding the samples into a powder, and microhardness measurements showed no gradient across the entire cross section. However, the position of the curve given in the present work does suggest a nonequilibrium condition exists in the carburized wires.

Experimental Measurements. For the determination of the tensile strengths, filaments were broken into 1-in. lengths and each piece was cemented onto flat plates, which had been scored so as to insure correct alignment of the sample. The flat plates constituted the end portions of the grips. The gage length of the samples was about 1/4 in. and the cross-head speed of the tensile tester was 0.02 in. per min.

A three knife-edge arrangement was used in the transverse-rupture test. The radii of the knife edges were 0.03 in., the gage length of the samples was 0.252 in., and the cross-head speed was 0.02 in. per min. The moduli were calculated by the usual beam formula:

$$\sigma = \frac{MC}{I_B}$$

where σ is the modulus of rupture; M, the moment; C, the neutral axis; and I_B the moment of inertia. For our purpose,

$$\sigma = \frac{\rho l}{\pi r^3}$$

where ρ is the load; l, the gage length; and r, the cross-section radius. In both the tensile and the bend experiments as many as ten pieces from each filament were tested. The microhardness measurements were made on the cross sections of pieces of the filament which had been mounted in plastic, polished, and etched. Two different loads were used, 25 g and 100 g. At least five indentures per sample were made. As many as fifteen indentures per sample were made on several specimens in order to check the uniformity of the cross section. In these cases the 25-g load had to be used.

The room-temperature electrical resistivities were determined potentiometrically. These measurements were made at various positions along the length of the filaments. The smallest distance between the voltage probes was 25 mm.

The Gouy method was used for the magnetic-susceptibility experiments. A 3- to 5-in. length of filament was suspended by a 5-mil-diam copper wire from a substitutional weight microbalance to the middle of a pair of 1-in.-diam pole caps of a 12-in. electromagnet. The air-gap between the pole caps was 1/4 in. A 3-in.-diam glass tube from the balance to the yoke of the magnet and a plastic shield around the entire yoke were provided to eliminate the effects of drafts while weighing. The yoke shield had a removable door for access to the sample. Electrostatic charges were eliminated by positioning strips of polonium-210, an α emitter of 500 microcuries, near the balance pan, the copper wire, and sample. Prior to turning on the current to the magnet, the polonium near the sample was removed so as not to perturb the magnetic field.

The sample was glued to the suspension wire by a very small drop of Canadian balsam. The balsam made no detectable contribution to the susceptibility. The maximum field was 36,000 gauss at 2.0 amp. Measurements were made at four different field strengths by varying the current of the magnet from 0.25 to 1.9 amp. The magnetic-field strength at the center of the pole caps and at the upper end of the specimen was measured directly with a rotating-coil gauss meter which had an accuracy of ±0.1 pct. The temperature of the room was kept constant at 25° ± 0.5°C. A plastic box of 1/2-in.-thick walls covered the microbalance to eliminate adverse effects due to the body heat of the operator. The light for illuminating the scale of the balance was turned on 2 hr prior to testing in order for the temperature within the box to come to equilibrium.

RESULTS

Color Change. A color transition was found to occur as a function of composition within the fcc phase. At low concentrations of carbon the color is a metallic silver. It changes to a slightly golden color between $TaC_{0.8}$ and $TaC_{0.85}$ and then to a bright gold at higher concentrations.

Resistivity Change. The change in resistivity during the reaction for various initial pressures of hydrocarbon expressed in terms of the final composition is given in Fig. 7. These resistivity values

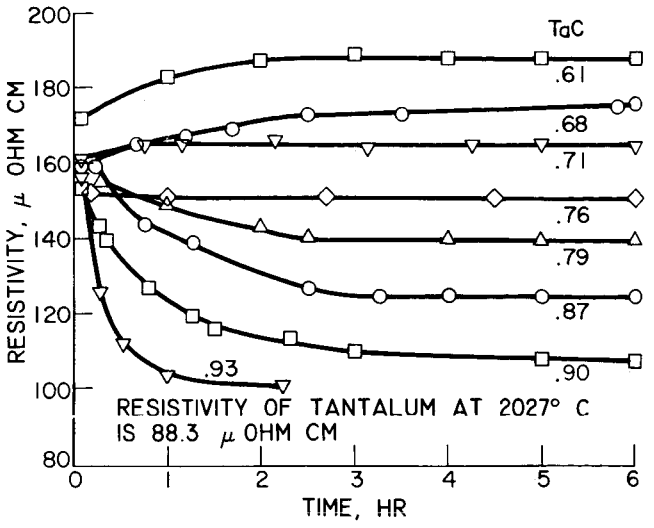

Fig. 7—Approximate resistivity at 2000°C during carburization for various initial hydrocarbon pressures expressed as final composition.

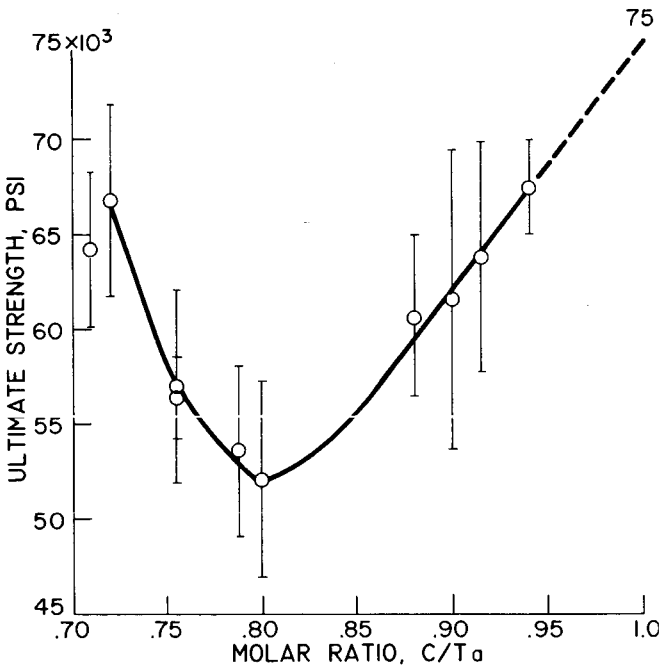

Fig. 8—Ultimate tensile strength of tantalum carbide. The center of the circles represent the mean strength values and the limits on each point represent the standard deviation.

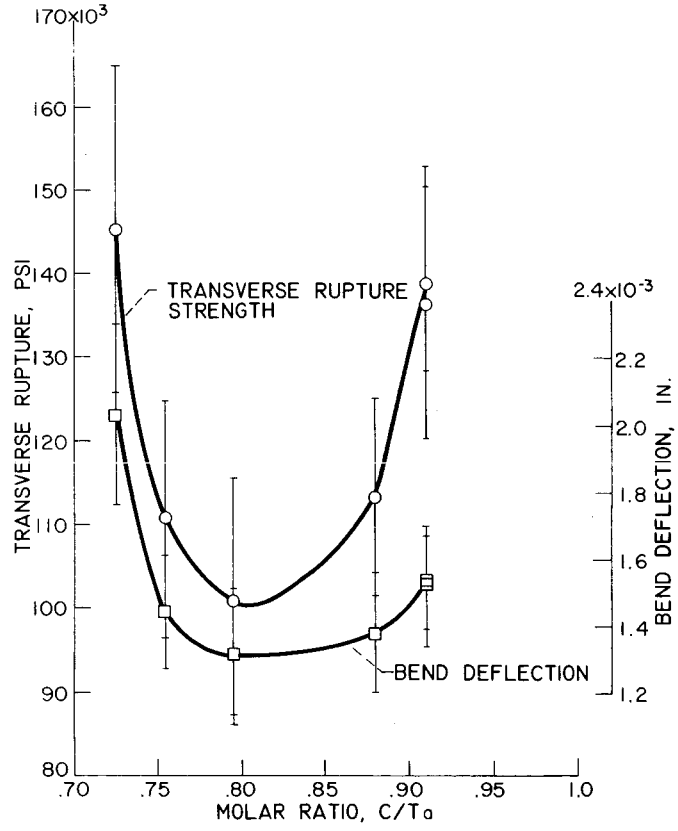

Fig. 9—Transverse-rupture strength and bend deflection of tantalum carbide. The center of the circles and squares represent the mean values and the limits on each point represent the standard deviation.

are only approximate due to the method used and the uncertainty in the wire dimensions at the high temperature. At higher pressures the resistivity quickly reaches a maximum and then falls rapidly to a fairly constant value. The greater the initial pressure, the more rapid is the decrease in resistivity. At lower pressures the resistivity also rises rapidly, but then instead of decreasing it continues to increase slightly. Between an initial pressure corresponding to a final product of $TaC_{0.71}$ and $TaC_{0.76}$ the resistivity remains relatively constant after the initial rise.

Tensile Strength. The tensile strength as a function of the composition for the fcc phase is given in Fig. 8. Although there is a great deal of scatter, a minimum in the curve can be observed at about $TaC_{0.8}$ with a value of 52,000 psi. An extrapolation of the curve to $TaC_{1.0}$ results in a tensile strength for that composition of 75×10^3 psi. Becker and Ewest[8] reported a value for the tensile strength of TaC of about 2800 to 4300 psi for a 1.2-mm-diam wire. Eckstein and Forman[9] report 30,000 to 35,000 psi with bulkier specimens, prepared by carburizing small pieces of tantalum. For the "as-received" electron beam-melted tantalum wires, the ultimate strengths were found to be 59,900 psi and for the other tantalum wire 59,400 psi.

Elongation data were not obtained since the test specimens had a tendency to slip in the grips. Not a single specimen, regardless of composition, displayed even the slightest plastic flow; nor did microscopic examination reveal the least necking down at the fracture.

Modulus of Rupture. In the transverse-rupture tests, both moduli of rupture and bend deflections were obtained and are shown in Fig. 9. In both of these curves a minimum occurs at about $TaC_{0.81}$ with a modulus of rupture value of 100,000 psi and a deflection of 1.30×10^{-3} in. Not enough data points were obtained near the high-carbide end of the curve to attempt an extrapolation to $TaC_{1.0}$, but at $TaC_{0.91}$ the modulus of rupture was 138,000 psi and the bend deflection was 1.55×10^{-3} in.

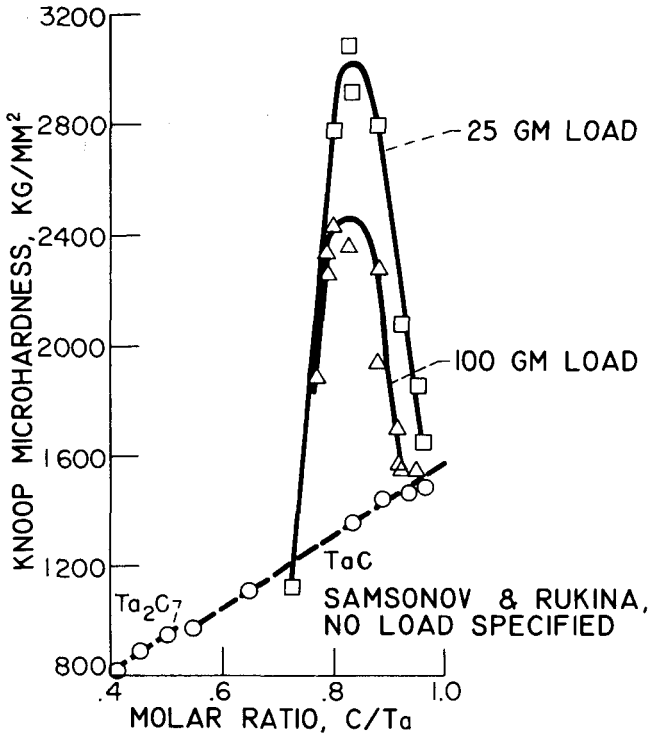

Fig. 10—Knoop microhardness of tantalum carbide.

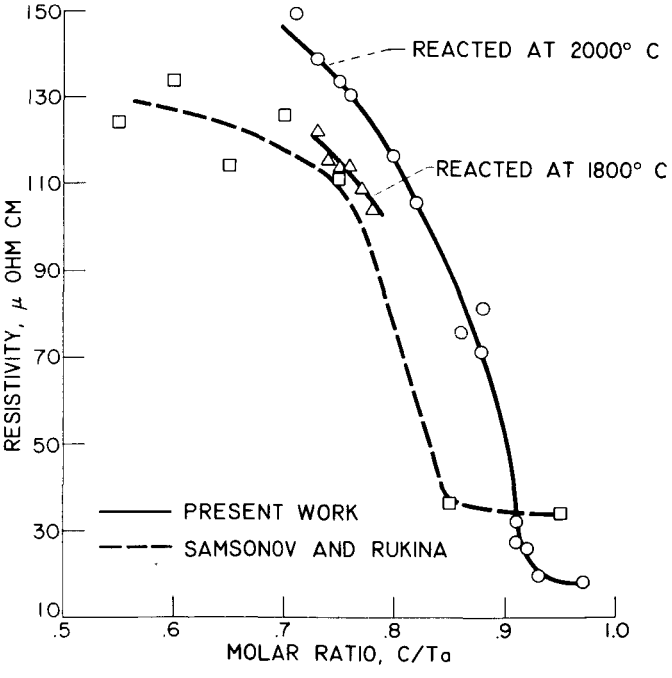

Fig. 11—Room-temperature resistivity of tantalum carbide.

Hardness. In Fig. 10 hardness data are given using a 25-g load and a 100-g load. A maximum in these curves occurs at between $TaC_{0.80}$ and $TaC_{0.85}$ which is near the composition where a minimum occurred in the tensile and the transverse-rupture tests. A hardness of 1650 kg per sq mm was obtained at $TaC_{0.96}$ using a 25-g load and of 1550 kg per sq mm at $TaC_{0.948}$ with the 100-g load. Since the hardness at $TaC_{0.915}$ and at $TaC_{0.92}$ (100-g load) were about the same as that for $TaC_{0.948}$, the curve was not extrapolated to $TaC_{1.0}$. Contrary to the results of this work, Samsonov and Rukina[1] have reported a nearly linear relationship for the microhardness for both the Ta_2C and the TaC phase regions, see Fig. 10. The authors did not specify what load they had used, but their values extrapolate to about 1600 kg per sq mm at $TaC_{1.0}$. A summary of microhardness values reported in the literature is given in Table III.

Table III. Review of Microhardness Data for TaC

Author	Date	Load, G	Microhardness, Kg Per Sq Mm	Composition, Molar Ratio C/Ta
Kieffer and Kolbl[17]	1949	50	1800	Assumed $TaC_{1.0}$
Foster and co-worker[17]	1950	—	1952	Assumed $TaC_{1.0}$
Hinnüber[17]	1950	20	1800	Assumed $TaC_{1.0}$
Mierson and Umanskii[10]	1953	—	1547	Assumed $TaC_{1.0}$
Samsonov and Rukina[1]	1957	—	980	0.545
			1340	0.820
			1450	0.935
			1580[a]	1.00

[a]Extrapolated.

Resistivity. Fig. 11 shows the room-temperature resistivity in the fcc phase. A similar effort by Samsonov and Rukina[1] is also given for comparison. The lowest value reported for the resistivity of TaC is 25 microhm-cm,[10] as compared to the value found here of 18.5 microhm-cm for $TaC_{0.97}$. A lower temperature of carburization (1800°C) appears to lower the room-temperature resistivity, at least for the lower carbides between $TaC_{0.73}$ and $TaC_{0.78}$. These latter data agree better with the Russian authors, who prepared their specimens at 1800°C. The room-temperature resistivity for the electron beam-melted "as-received" tantalum wire prior to carburization was found to be 13.7 microhm-cm, while that for the other wire was 13.5 microhm-cm. A literature value for the resistivity of tantalum is 12.4 microhm-cm at 25°C.[11]

The approximate resistivity for tantalum carbide at 2000°C after 6 hr reaction time is seen in Fig. 12 to vary linearly with composition. The extrapolated resistivity at 2000°C is 90 microhm-cm for $TaC_{1.0}$. Becker and Ewest[8] in 1930 reported the temperature variation of tantalum carbide between 1200° and 2400°K. Their value for the resistivity at 2000°C corresponds to a composition of about $TaC_{0.79}$ on the curve in Fig. 12. Recently Eckstein and Forman[9] have determined resistivities between 1400° to 3500°K, which, based on Fig. 12, corresponds to about $TaC_{0.76}$. Both sets of data were collected from specimens prepared from a solid-gas phase reaction, but exact compositions were not determined.

Magnetic Susceptibility. The magnetic-susceptibility variation with composition in the fcc phase is given in Fig. 13. A maximum diamagnetism occurs at about $TaC_{0.8}$. The transition from diamagnetism

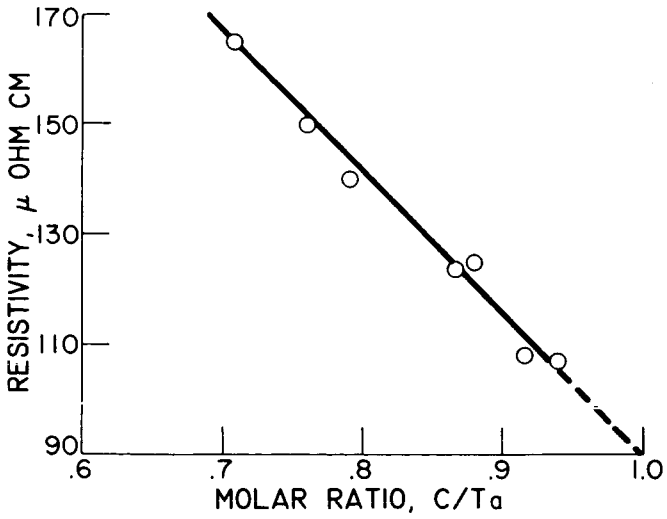

Fig. 12—Approximate resistivity of tantalum carbide at 2000°C. Reacted 6 hr.

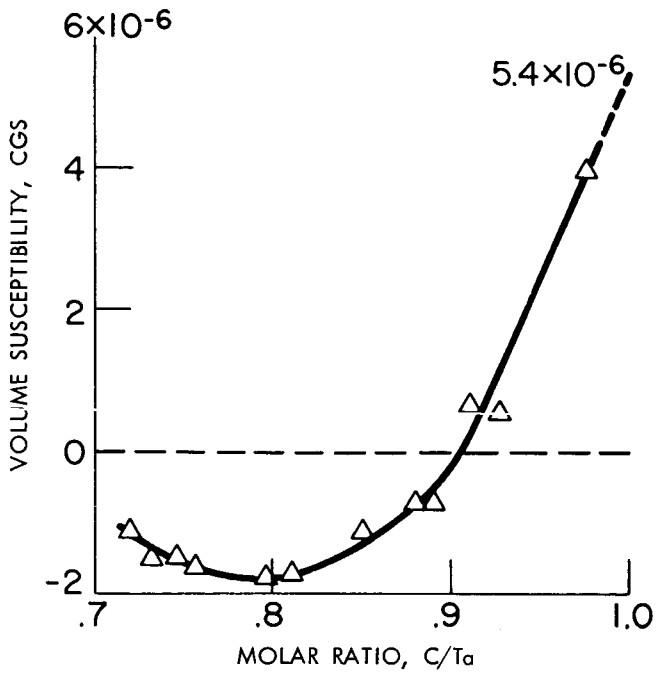

Fig. 13—Magnetic susceptibility of tantalum carbide.

to paramagnetism occurs at about $TaC_{0.9}$. An extrapolation to $TaC_{1.0}$ gives a volume susceptibility of $+5.4 \times 10^{-6}$ cgs units. It was not possible by this method to determine the susceptibilities of the "as-received" tantalum filaments since their susceptibilities were sufficiently large to cause them to stick to the pole face when the magnetic field was on. In fact, the long test specimens of the highest carburized samples were also affected in this way. Fortunately, by reducing their lengths and suspending them so that their upper ends were at the center of the pole caps, measurements could be made on the high-carbide filaments. None of the compositions displayed any variation of susceptibility with field strength, thus indicating an absence of ferromagnetic impurities.

Two other values reported for the volume susceptibility of a TaC are $< +6.53 \times 10^{-6}$ by Kelmm and Schüth[12] and $+0.70 \times 10^{-6}$ by Bittner and Goretski.[13] The latter authors[14] have just recently reported the molar susceptibility variation with composition in the TaC-phase. The qualitative agreement with the present work is good. They show a maximum diamagnetism at $TaC_{0.8}$ and a transition from diamagnetism to paramagnetism at $TaC_{0.9}$. However, the values here are higher than theirs by about a factor of seven for $TaC_{1.0}$ and a factor of two for $TaC_{0.8}$. Yet, it would be expected that the extrapolated value for $TaC_{1.0}$ found in this paper would be slightly low rather than high since the highest carburized specimens had been reacted in an excess of hydrocarbon vapor and had a carbon coating. As it was not possible to remove the last traces of this coating, its presence would tend to lower the positive force on the paramagnetic carbide, since graphite is highly diamagnetic.

DISCUSSION

As it has been shown here by the results of the X-ray diffraction, the photomicrographs, and the electrical resistivities, it is difficult to prepare tantalum carbide by a solid-gas phase reaction. Apparently the diffusion of carbon into a tantalum-carbide matrix is very slow. In spite of its drawbacks the gas-phase method of preparation is of interest since it provides a means of preparing complex-shaped hardware of tantalum carbide by first forming the piece out of tantalum and subsequently heating it in a hydrocarbon atmosphere. Brewer *et al.*[15] and Hörster and Kauer[16] have investigated the solid-gas phase reactions in tantalum carbide in some detail.

The color transition occurring in fcc TaC is related to the electronic structure which is altered by the addition of carbon atoms. This is in agreement with the maximum diamagnetism occurring at about the same composition as the color transition. Further, Giorgi and coworkers[7] found that the superconducting transition temperature, which is highest for $TaC_{1.0}$, is lowered with the decreasing carbon until at about $TaC_{0.85}$ it disappears, at least down to 1.05°K. It has also been speculated by Storms[10] that the maximum melting point in the phase diagram occurs at $TaC_{0.8}$. The evidence then seems to indicate that a transition in the electronic structure takes place at a critical composition somewhere between $TaC_{0.8}$ and $TaC_{0.85}$.

Whether or not such an electronic phenomenon is responsible for the maximum in the hardness and the minimum in the other mechanical properties reported here cannot be stated for certain, since these are so sensitive to macro effects. Further efforts concerning the mechanical properties of nonstoichiometric tantalum carbides are required before a more positive statement can be made. However, it is puzzling why the strength curves do not correspond with the hardness curve. Normally one would expect maximum hardness to coincide

with maximum strength. However, this reasoning stems from experience with materials exhibiting some degree of plasticity. Whether such behavior should be expected in the carbides is unresolved.

The utility of the tensile and the transverse-rupture data for direct engineering purposes is dubious for two reasons. The extrapolation of the data on filaments to larger bodies is questionable and microscopic examinations revealed that the test specimens contained microscopic surface cracks or notches, some of which extended to a considerable distance into the interior. It is to be expected then that higher values would result from sound bodies.

SUMMARY

A number of properties have been investigated in the fcc phase of the Ta-C system. It has been found that a maximum in microhardness, a minimum in tensile strength, a minimum in bend moduli and deflection, a maximum in diamagnetism, as well as a color transition occur between $TaC_{0.8}$ and $TaC_{0.85}$. It is thought that an electronic structural transition in this composition range is responsible for the color change and for the change in the slope of the susceptibility curve. It may also prove to be a factor in the shape of the mechanical-property curves.

Author

REFERENCES

[1]G. V. Samsonov and V. B. Rukina: Microhardness and Electrical Resistance of Tantalum Carbides in Their Homogeneous Region, *Dopovidi Akad. Nauk Urk. RSR*, 1957, no. 3, p. 247.

[2]V. I. Smirnova and B. F. Ormont: Limits of Homogeneity and the Relation of the Thermodynamic and Other Properties of the Carbide Phases of Ta to Their Composition and Structure, *Zh. Fiz. Khim.*, 1956, vol. 30, p. 1327.

[3]V. I. Smirnova and B. F. Ormont: Relation of the Heat and Free Energy of Formation of Tantalum Carbides to Phase and Chemical Composition, *Dokl. Akad. Nauk. SSSR*, 1955, vol. 100, p. 127.

[4]A. L. Bowman: The Variation of Lattice Parameters with Carbon Content of Tantalum Carbide, *J. Phys. Chem.*, 1961, vol. 65, p. 1596.

[5]R. Lesser and G. Brauer: Carbide Phases in Tantalum, *Z. Metallk.*, 1958, vol. 49, p. 622.

[6]R. T. Dolloff: Research Study to Determine the Phase Equilibrium Relations of Selected Metal Carbides at High Temperatures, National Carbon Research Laboratory Progress Report No. 3, December, 1962, pp. 13-17.

[7]A. L. Giorgi and co-workers: Effect of Composition on the Superconducting Transition Temperature of Tantalum Carbide and Niobium Carbide, *Phys. Rev.*, 1962, vol. 125, no. 3, p. 837.

[8]K. Becker and H. Ewest: The Physical Properties and Radiation Characteristics of Tantalum Carbide, *Z. Tech. Phys.*, 1930, pp. 148 and 216.

[9]B. H. Eckstein and R. Forman: Preparation and Some Properties of Tantalum Carbide, *J. Appl. Phys.*, 1962, vol. 33, no. 1, p. 82.

[10]E. K. Storms: A Critical Review of Refractories, Part I, Selected Properties of Group 4a, 5a, and 6a Carbides, LAMS-2674, Chem., TID-4500, 17th ed., Feb. 1, 1962.

[11]Tantalum and Tantalum Alloys, DMIC Report 133, p. 25, Battelle Memorial Institute, 1960.

[12]Wilhelm Kelmm and Wilhelm Schüth: Magnetochemical Investigation Concerning the Magnetism of a Few Carbides and Nitrides, *Z. Anorg. Allgem. Chem.*, 1931, vol. 201, p. 24.

[13]H. Bittner and H. Goretski: Magnetic Measurements on the Partial System: TiC-ZrC, TiC-HfC, ZrC-HfC, TiC-VC, TiC-NbC, TiC-TaC, and NbC-TaC, *Monatsh. Chem.*, 1960, vol. 91, p. 616.

[14]H. Bittner and H. Goretzki: Magnetic Investigation of the Carbides TiC, ZrC, HfC, VC, NbC, and TaC, *Monatsh. Chem.*, 1962, vol. 93, p. 1000.

[15]L. Brewer, D. Cooper, Jr., and G. Bird: Solid and Gas-Phase Reactions in a Tantalum Carbide Incandescent Light Source, presented August 10, 1961, at the XVII Congress of Pure and Applied Chemistry, Montreal, Canada.

[16]H. Hörster and E. Kauer: Investigation of the Kinetics of Gas-Solid Reactions by Means of Electrical Measurements, *Z. Elektrochem.*, 1962, vol. 66, p. 667.

[17]P. Schwarzkopf and R. Kieffer: *Refractory Hard Metals*, McMillan, New York, 1953.